

Mathematical Modeling of a Concrete Surface "Skin Effect" on Diffusion in Chloride Contaminated Media

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Concrete skin is considered the closest zone to the surface of concrete cover of reinforcements. It usually has a different composition than the internal concrete due to phenomena such as contact with molds or segregation of aggregates. In addition, environmental actions induce a gradient of moisture along the cover depth. These circumstances sometimes produce an irregular chloride profile in the cover, which either exhibits a maximum of chloride content some millimeters inside the outer surface or sometimes shows an anomalously high chloride concentration right at the concrete surface. In the present paper, analytical modeling of chloride diffusion is used to study the relative influence of the skin thickness. This theoretical analysis aims to show that there are cases where, if the diffusivity of the skin and the bulk concrete are very different, an error is introduced when the "skin effect" is not accounted for. The clarification of this error may contribute to understanding the differences found between laboratory experiments and the long-term record of chloride profiles in the same concrete. *ADVANCED CEMENT BASED MATERIALS* 1997, 6, 39–44. © 1997 Elsevier Science Ltd.

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Due to the increasing amount of damage noted in concrete structures located in marine environments or in contact with deicing salts, much more attention is being paid to the rate of chloride penetration through the concrete cover. The usual practice is to calculate chloride diffusivity values, D , from concentration profiles by curve fitting of a solution of Fick's second law [1,2]. For non-steady-state conditions and unidirectional flow in the x -direction, Fick's second law is [3]:

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1)$$

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where $C(x, t)$ is the chloride concentration at a point x at time t .

This equation can be solved by assuming: (a) a constant diffusion coefficient, D , and (b) the following conditions:

$$\text{Initial condition} \quad C(x, 0) = 0 \quad x > 0 \quad (2)$$

$$\text{Boundary condition} \quad C(0, t) = C_s \quad t \geq 0. \quad (3)$$

The solution to this boundary value problem is then:

$$C(x, t) = C_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{app}t}} \right) \right] \quad (4)$$

where $C(x, t)$ is the concentration at a depth x from the surface, C_s is the surface concentration during the time period considered, and D_{app} is the apparent diffusion coefficient (sometimes also called the effective diffusion coefficient).

In practice, this solution is fit to chloride profiles obtained either in cores taken from real structures or in specimens specifically tested in the laboratory. The D_{app} values so calculated are then used to predict chloride penetrations during longer periods.

However, in spite of the present wide use of this procedure, several attempts at a more rigorous model of chloride penetration [4–9] can be found in the literature. These attempts are based on the interpretation that the penetration mechanism of chlorides does not entirely fit into the initial and boundary conditions of eqs 2 and 3.

Among those authors who try to model boundary conditions other than those shown in eqs 2 and 3, Lin [4] addressed the modeling of two effects: (1) $C_s = f(t)$ is an exponential function of time; and (2) $D = f(t)$, where $f(t)$ is either an exponential or a polynomial expression. However, his solution contains numerous typographical errors that introduce doubt as to the reliability of the solution. Uji et al. [5] gave a mathematically correct solution for the case where C_s is a function of the square root of the time.

In a recent paper, Mangat and Molloy [6] stated that the application of Fick's second law assuming a constant D value is not an accurate procedure. From records of concretes in contact with salty ambient, they obtained a mathematical expression for the variation of diffusivity along the time: $D_c = D_i \cdot t^{-m}$. When this expression was introduced into the solution of Fick's second law, the D_i values obtained were on the order of $10^{-5} \text{ cm}^2/\text{sec}$, which seem too high, although Mangat and Molloy [6] justify this result.

The case of a variable surface concentration C_s existing in a delimited surface layer (skin) was studied by Masuda [7]. However, his solution assumes "washing" factors and air chloride contents that may not be of general application.

In a remarkable paper, Saelta et al. [8] addressed the subject of looking for nontraditional modeling of chloride penetration. They tried to model chloride ingress in either saturated or nonsaturated concrete using a numerical procedure based on the finite element method. They took into account the variability of chloride diffusion coefficients with concrete parameters such as degree of hydration, temperature, amount of evaporable water, porosity, and the chloride deposition rate on concrete surfaces. Assuming different mathematical expressions for the variation of these parameters, they solve the particular circumstances using the finite element method. Whether this numerical solution is correct or not must be elucidated by checking against different natural conditions other than those illustrated in the paper.

While it is relevant to point out that Saelta et al. [8] also modeled the case in which the chloride profile shows a maximum some millimeters inside the concrete surface. It appears in their model only when they dealt with chloride penetration in unsaturated concrete, where the concrete is not in contact with liquid water but is in an aerial marine atmosphere. That is, they consider that the maximum of chloride content inside the surface appears as a consequence of surface absorption-desorption phenomena.

However, a similar chloride profile pattern may appear if there is a "skin effect." Concrete skin is considered the layer closest to the surface. It has already been recognized [10] that the "skin" usually has a different composition than the concrete bulk. Reasons for the formation of the gradient in composition from the surface are: (a) the border or wall effect introduced during casting, which causes more paste/mortar to accumulate near the external border of the concrete; (b) concrete carbonation; or (c) the precipitation of brucite [11] formed during contact of hydrated cement with sea water. A skin effect can also be present when the concrete is coated by an overlay or paint [12].

In spite of the general acceptance of the existence of this skin effect, it is seldom considered in the literature when eq 4 is used. The present paper tries to show how the

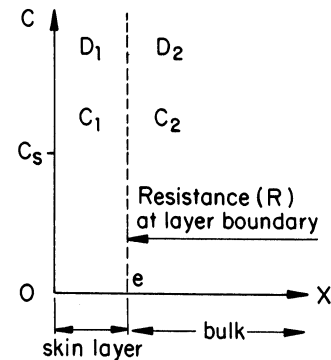


FIGURE 1. Recognition of two layers in the concrete surface: skin and bulk. D_1 , D_2 = diffusion coefficients; C_1 , C_2 = chloride concentration varying along the cover depth, x ; C_s = chloride surface concentration; R = resistance.

existence of this skin may influence the chloride profiles by means of some examples, where: (1) the definition of the specific mechanism of chloride penetration is not needed; (2) two diffusion coefficients instead only one are considered; and (3) an analytical mathematical solution is used. The subject is therefore addressed in a different manner than presented by Saelta et al. [8].

Mathematical Modeling

Fick's second law taking into consideration a two-layered interface (skin and bulk) has been solved [3]. Figure 1 represents the situation where D_1 is the diffusivity in the skin layer, D_2 is the diffusion of the interior part of the concrete, and the resistance of the interface is denoted by the resistance, if any, between the two layers.

The solution is reached by assuming the following conditions [3]:

$$\text{Initial} \quad C_1(x, 0) = 0 \quad 0 < x < e \quad (5)$$

$$C_2(x, 0) = 0 \quad x > e$$

$$\text{Boundary} \quad C_1(e, t) = C_2(e, t) \quad t \geq 0 \quad (6)$$

$$C_1(0, t) = C_s \quad t \geq 0.$$

The resulting solution is:

$$C_1(x, t) = C_s \sum_{n=0}^{\infty} \alpha^n \left(\operatorname{erfc} \left[\frac{2ne + x}{2\sqrt{D_1 t}} \right] - \alpha \operatorname{erfc} \left[\frac{(2n+2)e - x}{2\sqrt{D_1 t}} \right] \right) \quad (7)$$

$$C_2(x, t) = \frac{2kC_s}{k+1} \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc} \left[\frac{(2n+1)e + k(x-e)}{2\sqrt{D_1 t}} \right] \quad (8)$$

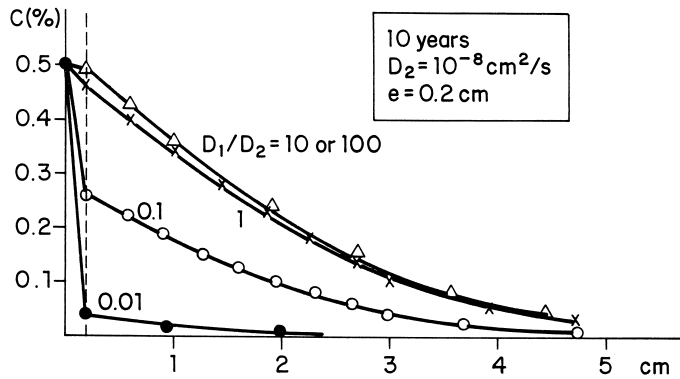


FIGURE 2. Influence of the variation of D_1/D_2 ratio on the chloride profiles for a cover thickness of 0.2 cm.

$$k = \sqrt{D_1/D_2}, \quad \alpha = \frac{1-k}{1+k}.$$

A “resistance,” R , between the two layers may also exist and, as a consequence, introduced into eq 1 results in new boundary conditions:

$$C_1(0, t) = C_s \quad t \geq 0 \quad (6')$$

$$C_1(e, t) = RC_2(e, t) \quad t \geq 0$$

and a new solution for C_2 :

$$C_2(x, t) = \frac{2kC_sR}{k+1} \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc} \left[\frac{(2n+1)e + k(x-e)}{2\sqrt{D_2t}} \right] \quad (9)$$

Results

Equation 9 has been implemented in a computer to obtain an analysis of the influence of each parameter. Thus, the variables analyzed were: (a) D_1/D_2 ratio, (b) skin thickness, (c) absolute value of the bulk diffusivity, and (d) considering a resistance, R , at the boundary between the skin and the bulk concrete.

Influence of D_1/D_2 Ratio

Values of $D_1/D_2 > 1$ may appear when, for instance, the skin is carbonated. Also, D_1 may be greater than D_2 when the chloride penetrates by capillary suction, which is known to result in faster penetration rates. The opposite case, $D_1 < D_2$, may be found when some barrier effect is built up at the surface, for instance, when brucite [8] precipitates there [14] or when paint coats the concrete surface [12].

Figure 2 shows the chloride profiles when assuming a skin of 0.2 cm thickness, for D_1/D_2 ratios of 0.01, 0.1, 1, and 100×. The resistance, R , between skin and bulk is assumed to be unity in these examples. The

ratio of $D_1/D_2 = 1$ may be used for comparative purposes with eq 4.

It can be deduced that only D_1/D_2 ratios < 1 would induce significant deviation from chloride profiles obtained from eq 4. Thus, the fitting of eq 4 to chloride profiles for D_1/D_2 ratios of 0.1 or 0.01 may give values of D (the value obtained from eq 4) that are one or two orders of magnitude smaller than D_2 (10^{-8} cm²/s in Figure 2), depending on whether the surface chloride concentration C_s is considered or the fitting starts at 0.2 cm (the skin is neglected), respectively.

Influence of Skin Thickness

This difference from fitting eq 4 or 9 is more evident when the skin presents a greater thickness, as shown in Figure 3 (again, R is assumed to be the unity). This figure represents different D_1/D_2 ratios, but with thicknesses of 0.1 or 1 cm. The thicker the skin, the more important is the influence of the D_1/D_2 ratio. Thus, differences are also found for D_1/D_2 ratios > 1 , particularly for $e = 1$ cm.

The fitting of eq 4 to these profiles would give a deviation of D with respect to D_2 of one or two orders of magnitude. That is, the difference of fitting eq 4 or 9 into these profiles is more important as the skin becomes thicker. For D_1/D_2 ratios < 0.1 , if the skin is thicker than 1 cm, the chloride penetration will be small beyond the boundary between the two layers.

Influence of Absolute Value of D_2

Theoretical chloride profiles for D_2 values of 10^{-7} , 10^{-8} , and 10^{-9} cm²/s are presented in Figure 4 (top panel) for a skin thickness of 0.2 cm, and in the bottom panel of Figure 4 for a skin thickness of 1 cm. These two cases are studied for D_1/D_2 ratios of 100 and $R = 1$.

The trend of the chloride profiles in the concrete bulk is as expected: sharper for low values of D_2 and flatter for the higher ones. The trend is maintained for thicker skins (bottom panel). Other examples with D_1/D_2

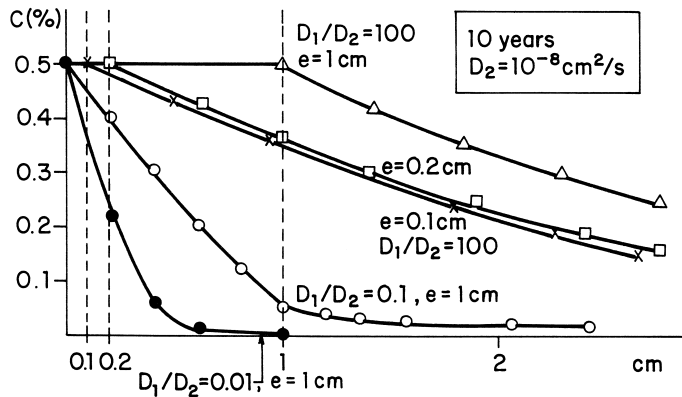


FIGURE 3. Influence of concrete skin thickness (0.1–0.2 or 1 cm) on chloride profile shape for several D_1/D_2 ratios.

smaller than 100 were not made, as the trend of the profiles can be deduced from Figures 2 and 3.

If eq 4 is fitted to the profiles shown in Figure 4, differences of D with respect to D_2 up to one order of magnitude can be found.

Effect of a Resistance Between Skin and Bulk

Up to now, it has been assumed that the resistance between the two layers was unity ($R = 1$). However, this R may be higher or lower. A physical explanation may be that R may represent a different ability to bind chlorides in the skin and in the bulk. This would be the case in a carbonated layer (skin). In such a situation, the

carbonated phases have no binding capacity and, as a result, an apparent maximum in total chlorides may appear just at the boundary. This would only represent that the free chlorides persist in the skin, and bound plus free chlorides are measured from the boundary to the interior. This phenomenon can be mathematically modeled by assuming $R > 1$ and $D_1 > D_2$.

An opposite situation may exist when $R < 1$, which would be the case in the presence of a coating [12]. Here, not only is $R < 1$, but mainly $D_1 < D_2$.

Therefore, the existence of a resistance, R , between skin and bulk has to be considered in addition to the D_1/D_2 ratio. Figure 5 presents chloride profiles for R

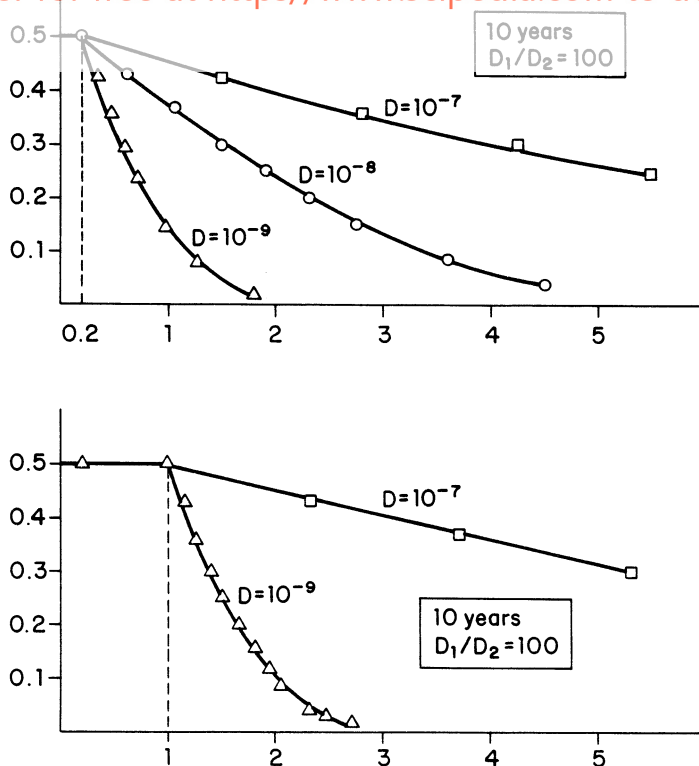


FIGURE 4. Influence of the variation of D_2 on the chloride profile for $D_1/D_2 = 100$. Top panel: 0.2 cm skin thickness; bottom panel: 1 cm skin thickness.

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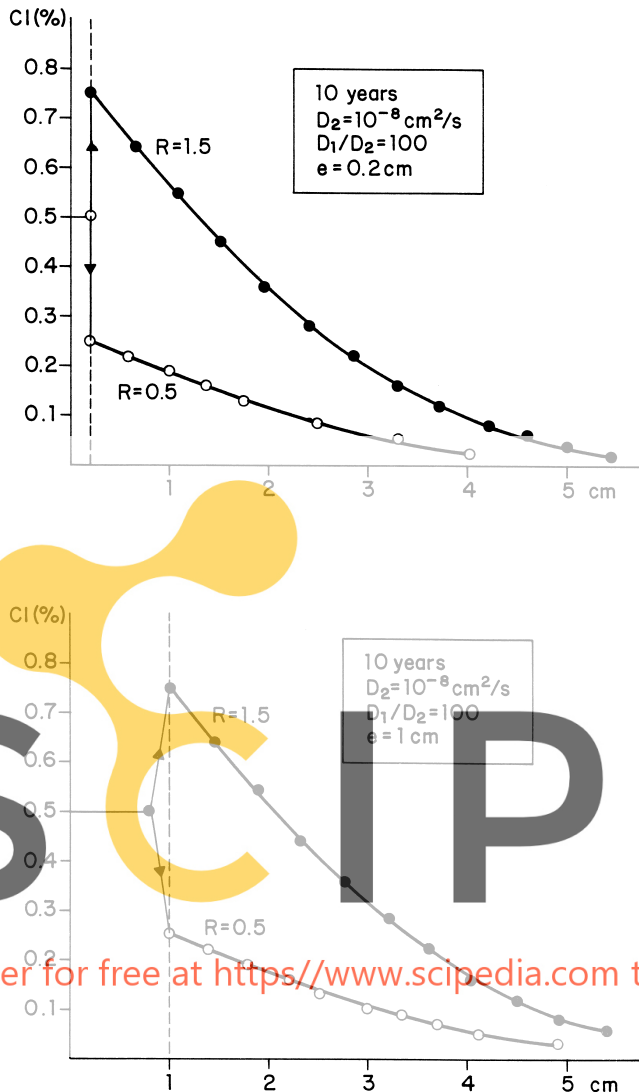


FIGURE 5. The existence of a “resistance” between skin and bulk also influences the chloride profile. Top panel: skin thickness of 0.2 cm; bottom panel: skin thickness of 1 cm.

values of 0.5 and 1.5 and for skin thicknesses of 0.2 cm (top panel) and 1 cm (bottom panel), with $D_1/D_2 = 100$ and $D_2 = 10^{-8} \text{ cm}^2/\text{s}$. If eq 4 is fit to these profiles, differences in the fitted value of D up to one order of magnitude from D_2 can be found. This difference between fitting eq 4 or 9 is more important for thicker skins and lower D_2 values. In these cases, not considering the skin in the fitting exercise will result in significant deviations of the D values.

Discussion

Chloride profiles that apparently do not fit well into Fickian behavior are often noted [13] in cases of profiles presenting a maximum some millimeters inside the

concrete surface. These profiles are usually attributed to surface absorption-desorption phenomena in the aerial parts of the structures or to washing effects of rain. However, they could be also generated due to the existence of a concrete skin having a different composition than that of the bulk.

When they are noted, usually their trend in the skin is neglected and the maximum is extrapolated towards the surface by simply applying eq 4. However, the present results have attempted to show that this procedure may give erroneous results for the diffusion coefficient in the concrete bulk if certain circumstances exist. Thus, considering the examples given in Figures 2 through 5, it can be deduced that the existence of a skin may lead to significant deviations of the classical error function solution in the following cases:

1. If the skin is thick (for instance, $>0.5 \text{ cm}$), and:
 - $D_2 < 10^{-8} \text{ cm}^2/\text{s}$
 - $D_1/D_2 > 1$
 - there is a resistance at the bulk boundary.
2. If the skin is thin (only a few millimeters), and:
 - $D_1 < D_2$
 - there is a resistance at the bulk boundary.

The different resistance (binding ability of cement phases towards chlorides, for instance) between skin and bulk seems to be one of the most influential parameters producing such a difference.

The existence of resistance with different behavior in the bulk may also be one of the reasons for the reported decrease of the chloride diffusion coefficient as time proceeds [13]. Thus, it seems reasonable to think that the influence of the skin may evolve with time (for instance, if it is due to carbonation), and, as a result, the chloride profiles would evolve as well from a “non-skin” shape to a “skin” shape.

However, from this hypothesis it cannot be concluded that the skin effect can justify all the reported deviations from a pure “error function profile” [14]. Other parameters, such as progressions of hydration or nonlinear binding ability [15,16] or climatic cycles, may also play an important role. Their relative influence has to be studied in greater detail in the future to clarify the entire mechanism of chloride penetration into concrete.

Conclusions

Among the different phenomena producing the chloride profile shape, in the present paper the “skin effect” has been analytically modeled and some examples have been provided for illustration. From the results, the following conclusions may be drawn:

1. The existence of a skin having a different chloride diffusivity than the bulk may result in different chloride profiles than those obtained from the usual solution of Fick's second law, that is, when the surface concrete layer has the same behavior as the bulk.
2. If comparison is made with chloride profile shapes given by this traditional solution of Fick's second law, skins 10 mm or thicker may be enough to alter the chloride profile shapes if D_1 (in the skin) is very different from D_2 (in the concrete bulk).
3. Chloride profiles presenting a maximum some millimeters beyond the concrete surface can be modeled by the arbitrary assumption that the binding ability of cement phases towards the chlorides is represented by a resistance, R , between skin and bulk higher than unity. Carbonated layers would be an example of lower chloride binding capacity in comparison with the uncarbonated bulk.

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